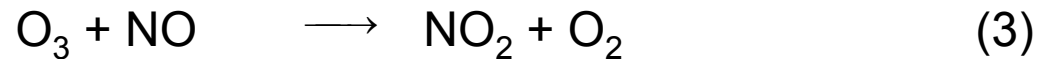
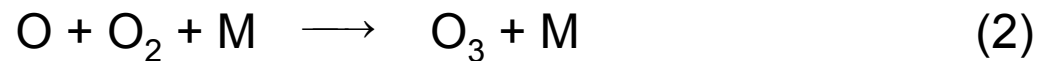
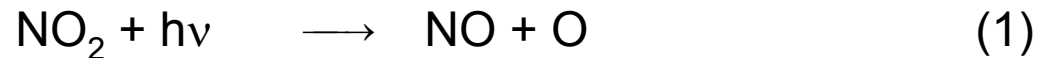


CHEMISTRY OF OZONE FORMATION IN THE ATMOSPHERE

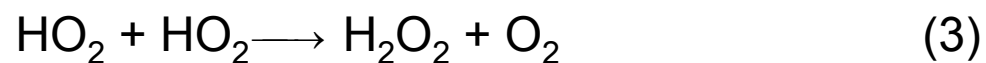
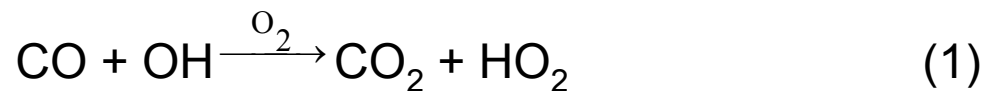
1. Basic Photochemical Cycle of NO₂, NO, and O₃

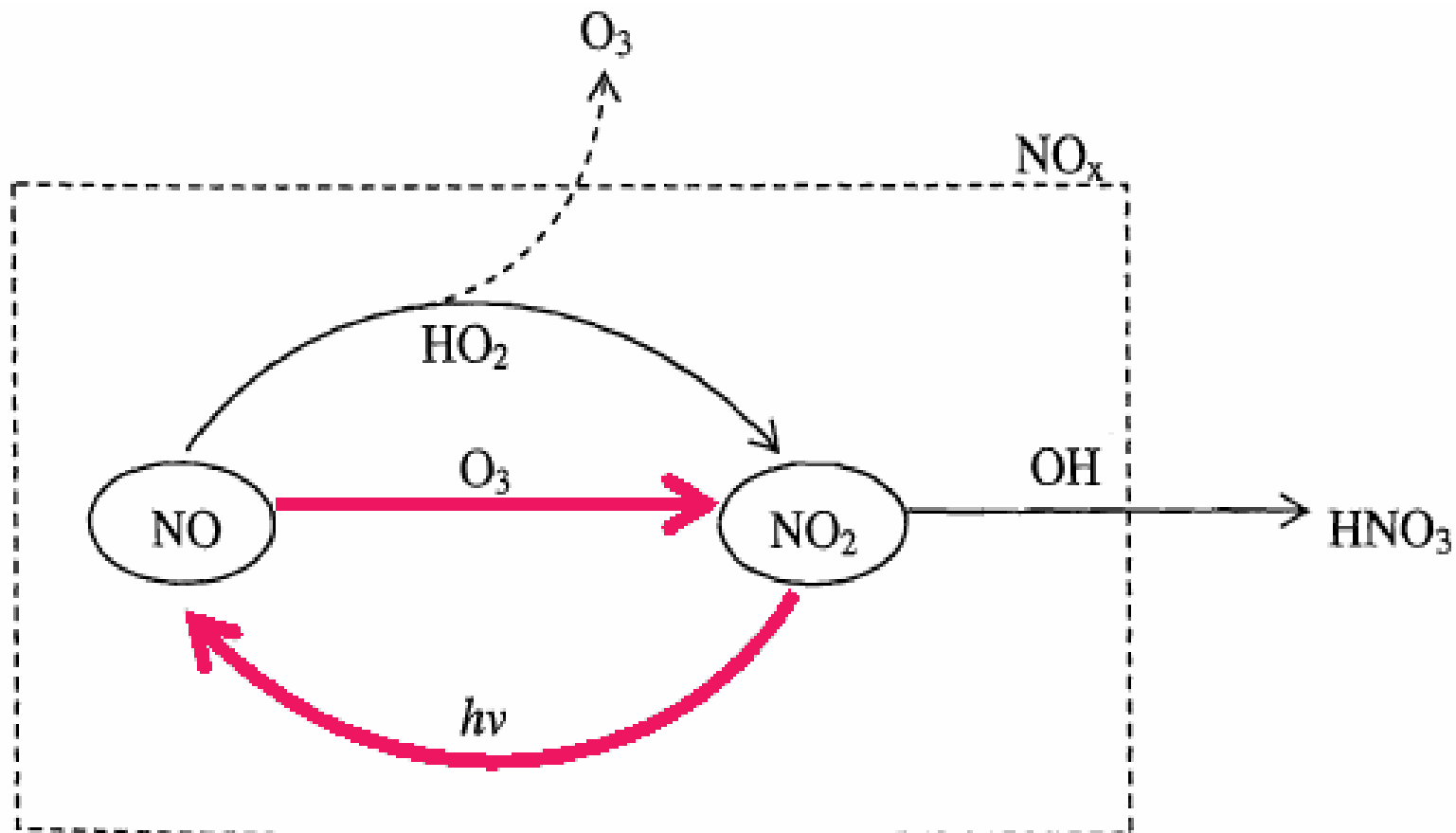


These reactions occur relatively rapidly so that a steady state is reached, in which the ozone concentration is

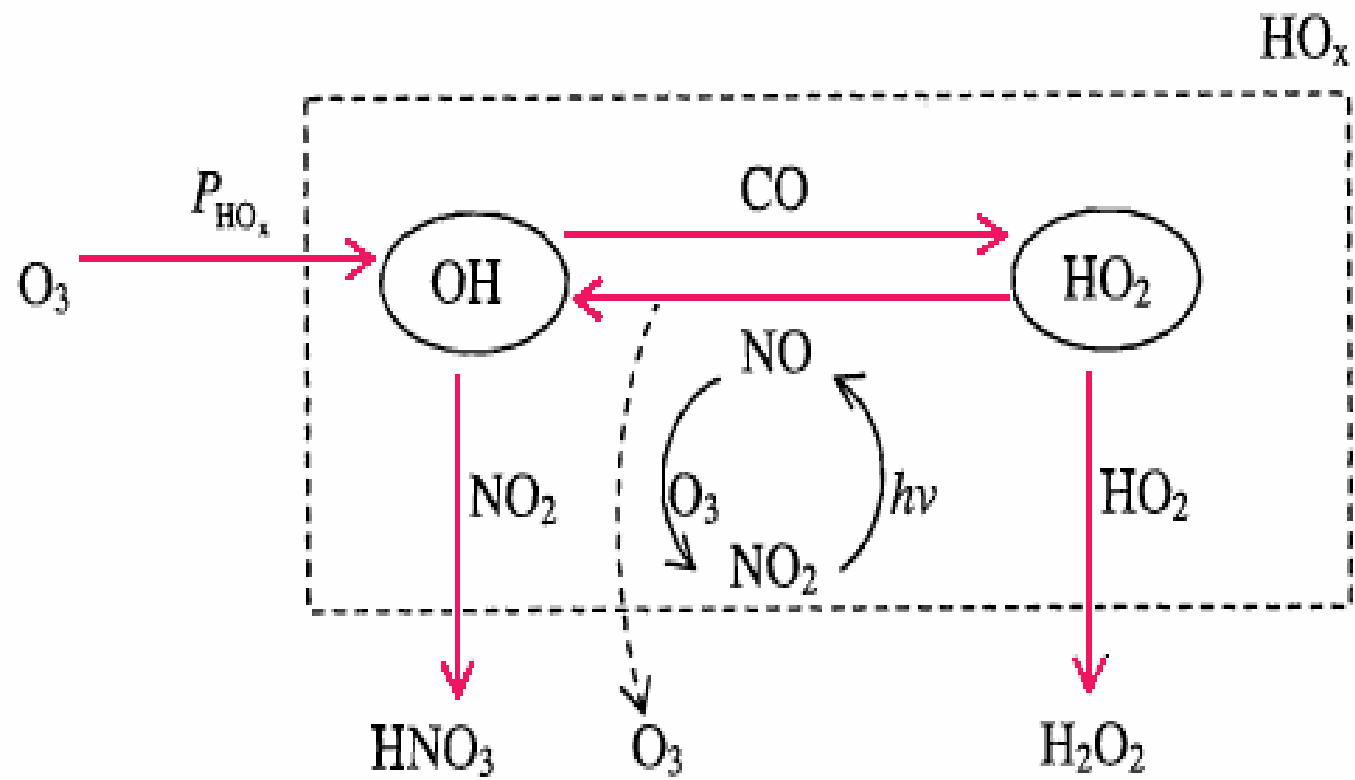
$$[\text{O}_3] = \frac{j_{\text{NO}_2} [\text{NO}_2]}{k_3 [\text{NO}]}$$

2. Atmospheric Chemistry of Carbon Monoxide





$$P_{O_3} = k_{HO_2+NO} [HO_2][NO]$$



3. Dependence of O₃ Formation on NO_x

Low NO_x Limit

Principal sink of HO_x is HO₂ + HO₂

$$P_{O_3} \sim [NO] \quad \Leftarrow \text{As } NO_x \uparrow, P_{O_3} \uparrow$$

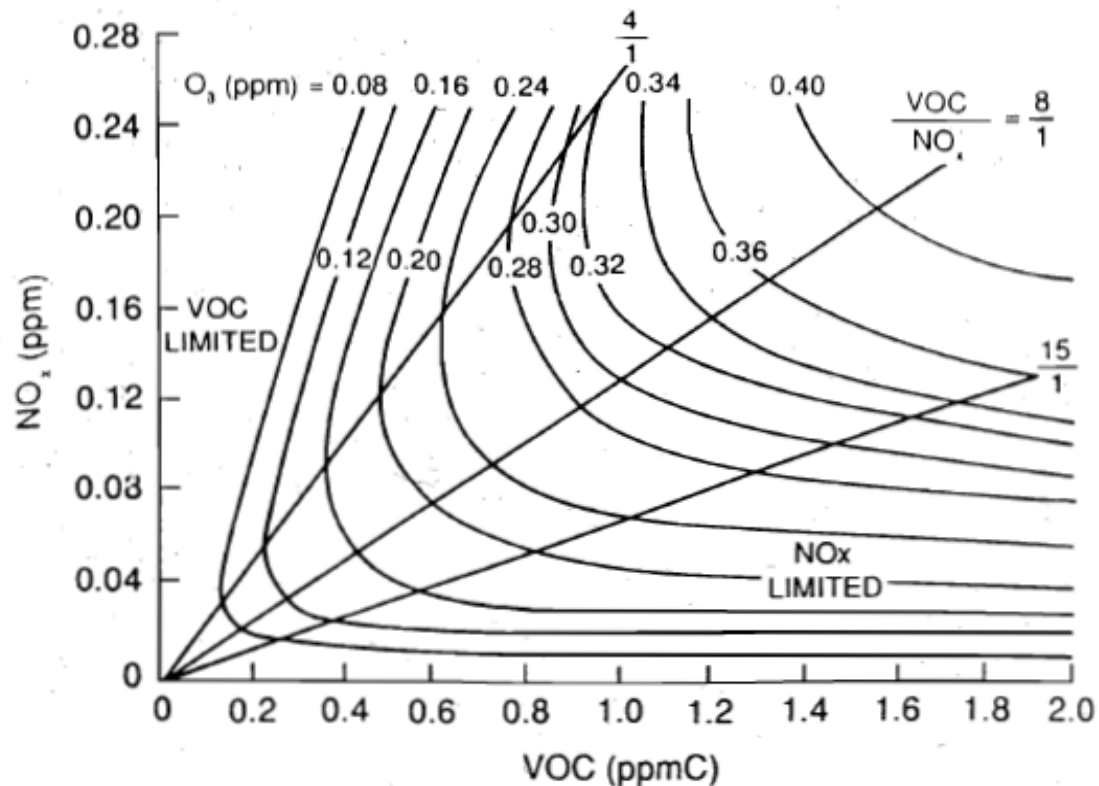
High NO_x Limit

Principal sink of HO_x is OH + NO₂

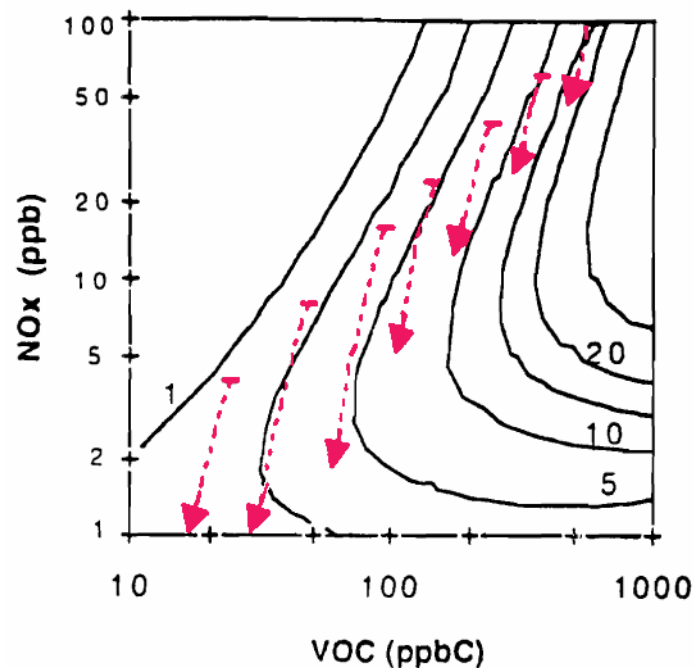
$$P_{O_3} \sim [CO]/[NO_2] \quad \Leftarrow \text{As } NO_x \uparrow, P_{O_3} \downarrow$$

4. Ozone Production Efficiency

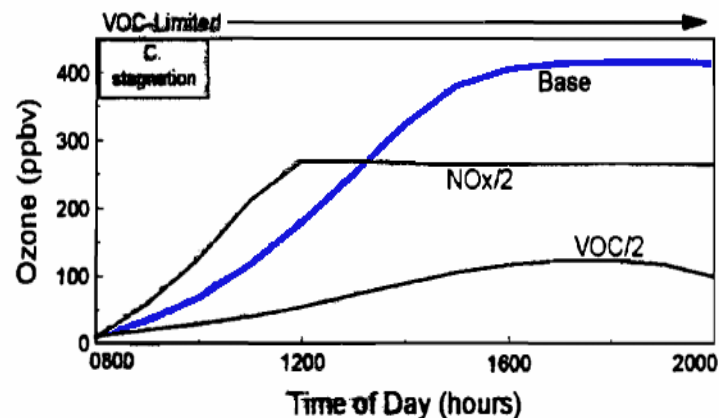
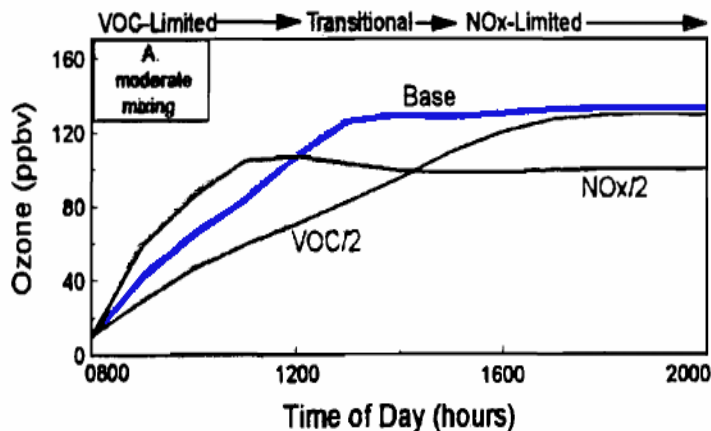
$$\text{OPE} = \frac{P_{\text{O}_3}}{L_{\text{NO}_x}}$$



Typical ozone isopleths used in EPA's EKMA. The NO_x limited region is typical of locations downwind of urban and suburban areas, whereas the VOC-limited region is typical of highly polluted urban areas.
 Source: Adapted from Dodge, 1977.



Isopleths giving net rate of ozone production (ppb/h, solid lines) as a function of VOC (ppbC) and NO_x (ppb) for mean summer daytime meteorology and clear skies. The solid lines represent production rates of 1, 2.5, 5, 10, 15, 20 and 30 ppb/h. The dashed lines and arrows show the calculated evolution of VOC and NO_x concentrations in a series of air parcels over an 8 h period (9am – 5pm), each with initial VOC/NO_x = 6 and speciation typical of urban centers in the US, based on calculations shown in Milford et al. (1994)



Simple model calculations illustrating the varying sensitivity of O_3 photochemical production to VOC and NO_x . In each panel, model-calculated O_3 concentrations are plotted as a function of time of day for a hypothetical air parcel containing an initial, urban-like mixture of anthropogenic VOC and NO_x under summertime conditions with 1 ppb of biogenic isoprene and varying rates of vertical mixing and free tropospheric entrainment. For each mixing rate, simulations for three initial VOC and NO_x concentrations are presented: “Base” with initial VOC and $NO_x = 1.5$ and 0.25 ppm respectively; “VOC/2” with initial VOC = 0.75 and $NO_x = 0.25$ ppm; and “ $NO_x/2$ ” with initial $NO_x = 0.125$ and VOC = 1.5 ppm. Note the characteristic tendency for the system to evolve from VOC-limitation to NO_x -limitation with time for the point of transition to be delayed as mixing decreases.